MODIS
Terra - Phytopankton Pigments
Data Quality Summary - August 2001

Investigation:	TERRA/MODIS
Data Product:	Product number - MOD 19: Parameter number - 13, Name - CZCS_pigment Parameter number - 14, Name - chlor_MODIS Parameter number - 15, Name - pigment_c1_total
Data Set:	Terra
Data Set Version:	3.1.3 and 3.2.1
Principal Investigator:	D. K. Clark

Nature of the products

A generalized discussion of this product and these three parameters can be found in the MODIS ATDB 18, Bio-optical Algorithms - Case 1 Waters, which is available at: http://modarch.gsfc.nasa.gov/MODIS/ATDB/atdb_mod18.pdf. However, that document does not cover recent changes to the algorithms implemented in data processing versions 3.1.3 and 3.2.1. One of the most significant modifications was to eliminate the in-water measurements acquired in high pigment concentration waters obtained using large diameter instruments. Strong absorption at shorter wavelengths produces large uncertainties in the measurements of the upwelled spectral radiances ($L_u(z)$) induced by instrument self-shadowing effects. This uncertainty is analogous to the long wavelength case modeled by Gordon and Ding (1992). The net effect, when computing blue to green band ratio, is to reduce the slope of the radiance ratios to pigment concentration relationships resulting in under estimating the pigment retrieval. High pigment concentration observations have been replaced by measurements acquired with fiber-optic instruments. Although originally these product parameters were developed for case 1 waters, this modification has produced empirical results which are theoretically consistent and can be utilized for Case 1 & 2 waters with increased accuracy.

The second modification to the ATDB addresses the problem of constraining the least-squares regression‘s extrapolation to the very low concentrations (for which there is a paucity of observations, i.e. pigments ranging between 0.01 to 0.05 mg/m3). This was accomplished by using ratios of the normalized water-leaving radiance for pure sea water computed by Howard Gordon.

Gordon's approach was to compute the normalized water-leaving radiances $nL_w(\lambda)$ (Gordon and Clark, 1981) as a limit for very low-chlorophyll water, free of particles and dissolved material over the spectral range $400 \leq \lambda \leq 750$ nm. The pure sea water nL_w's were calculated by combining the latest measurements of the absorption coefficient of pure water (Pope and Fry, 1997) and direct measurements of the spectral variation of the Raman scattering coefficient (Bartlett et al., 1998) with Monte Carlo simulations as described in Gordon (1999). An aerosol-free, purely Rayleigh-scattering atmosphere was used in the simulations. Aerosols at concentrations typical of those over the open ocean would have a negligible affect on the $nL_w(\lambda)$.

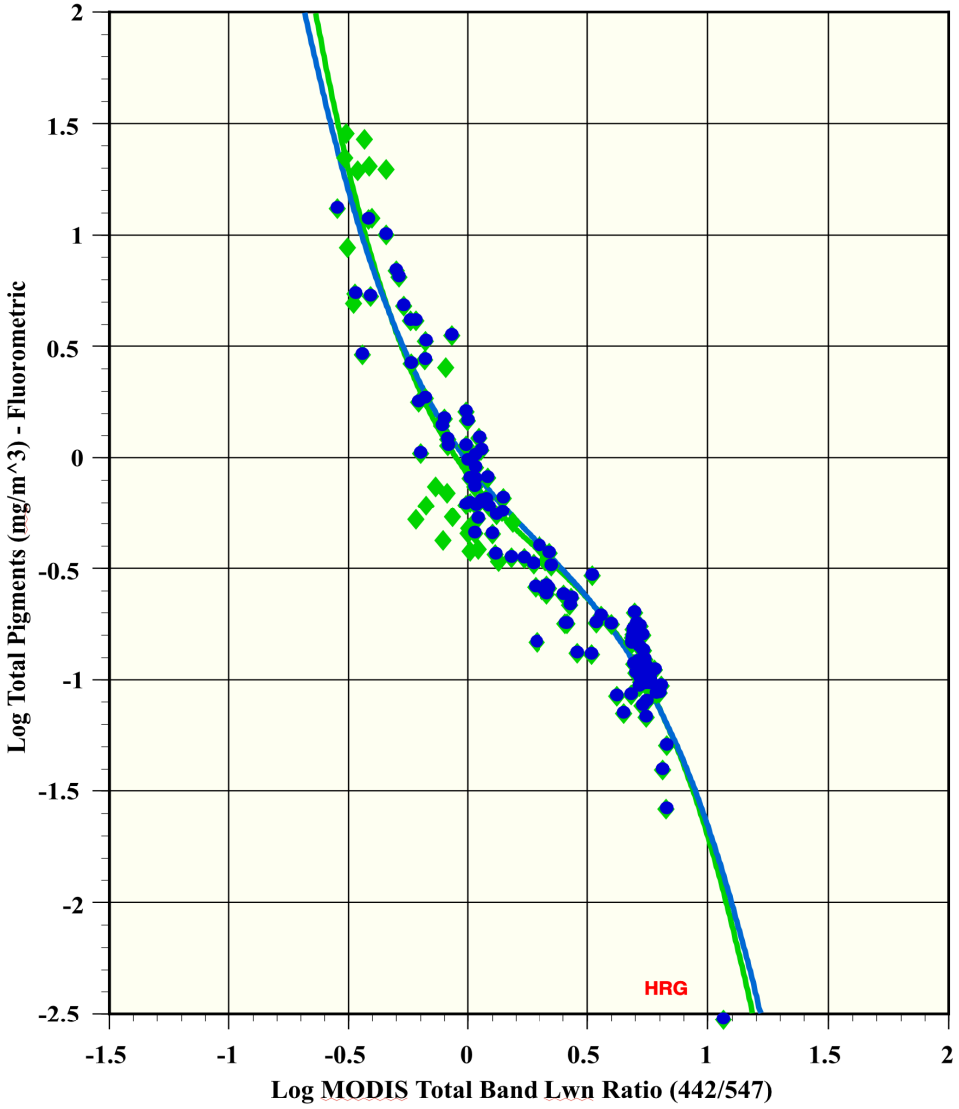

Figure 1. MODIS product-13, MODIS total band normalized water-leaving radiance ratios vs fluorometrically determined pigment concentrations (mg/m^3) with regression lines for case 1 waters (blue) and case 1 & 2 (green) waters.

The resulting data set of log MODIS total band averaged nL_w's for the 442 to 547 nm ratios vs. the log of the total fluorometric pigments (chlorophyll *a* plus phaeopigments) scatter plot is illustrated in Figure 1 . Observations in case 1 waters are plotted in blue with case 1 & 2 in green. The 3rd order polynomial regression results are plotted in the same respective colors with the pure sea water ratio value designated by HRG. The small difference between the curve fits for case 1 and case 1 & 2 data allows for the case 1 & 2 form to be used with out a significant increase in uncertainty. The parameters 14 and 15 results, while based on a smaller HPLC data sets, are consistent with this example.

The bio-optical data used in these analyses consists of the original NIMBUS-7 CZCS and the MODIS Marine Optical Characterization Experiment (MOCE) team's cruises for algorithm development. The geographical distribution of the bio-optical stations in this data set is illustrated in Figure 2.

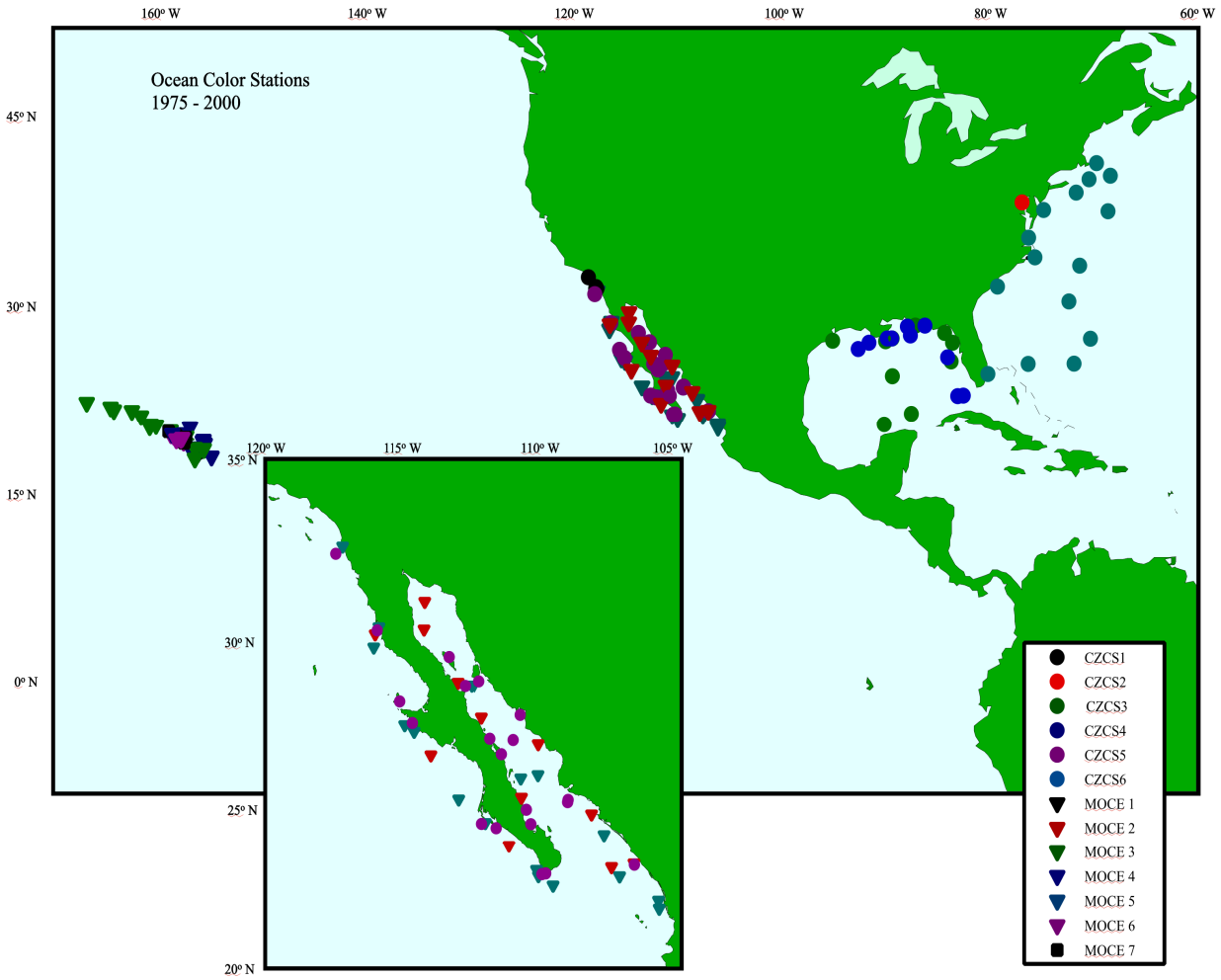

Figure 2. Station location map for the observations used in development of these products.

The generalized form for computing these MODIS pigment products is:

$$\text{Log Product} = (A(\text{Log X}))^3 + B(\text{Log X})^2 + C(\text{Log X}) + D) / E$$

Where:

A,B,C,D are least squares regression coefficients,

E is a constant for offsetting the derived relationship (presently set to 1),

X = [(e) nL_w (band 9) + (f) nL_w (band 10) + (g) nL_w (band 11)] / nL_w (band 12),
The wavelength bands 9, 10, 11, & 12 are centered at 442, 487, 530, & 547 nm, respectively.

e, f, and g are set to zero or one to select band combinations,

nL_w = MODIS total band solar normalized water-leaving radiance.

Product descriptions:

Product 13 - This pigment product is the sum of the chlorophyll *a* pigment and its degradation products, phaeopigments The product provides a basis for comparison to the heritage pigment algorithms developed for the Nimbus-7 Coastal Zone Color Scanner (CZCS) (Clark,1980, Gordon and Clark, 1983). Although both are based on pigment observations determined with the same fluorometric techniques (a single pigment compound measurement) and the same formulation of nL_w 's, there are differences. The CZCS used the nL_w 440/550 ratio for pigments < 1.5 mg/m^3 (case 1 water) and switched to an nL_w 520/550 ratio for pigment concentrations > 1.5 mg/m^3 (case 1& 2 water). This band ratio change was primarily required by the low signal to noise inherent in the CZCS instrument. MODIS products, with the instrument's high signal to noise ratio and increased digitization level coupled with the modifications to the base in-water algorithms, should be capable of spanning the nominal range of 0.01 to 20 mg/m^3. The equation for computing Product 13, CZCS_pigment (illustrated in Figure 1) is:

$$\text{Log Pigments} = -1.742 (\text{b9/b12}))^3 + 1.625 (\log (\text{b9/b12}))^2 - 1.495 \log (\text{b9/b12}) - 0.0794$$

The regression statistics for this analysis are: number of observations, n = 93 , coefficient of variance $r^2 = 0.912$, and the standard error of estimate $Sy \bullet x = 0.045$, k = 1.

Product 14 - This pigment product has been derived with the same approach as previously discussed in parameter 13, but differs in that the chlorophyll *a* and the derivative chlorophyll *a* pigment compounds are measured with HPLC techniques. The compounds, Chl *a* (monovinyl and divinyl), Chl *a* allomer, Chl *a* epimer, and chlorophyllide *a* were summed to form a total chlorophyll

a (TCHLA) and used in the nL_w regression analysis. The Chl *a* epimers and allomers are artifacts of the extraction process and chlorophyllide *a* is either a precursor compound to Chl *a*, a degradation product of Chl *a* in senescent cells, or an artifact of the extraction process (Trees *et al*., 2000). The nL_w ratio uses the Chl *a in vivo* absorption maximum in the Soret band near 442 nm to the 547 nm band (as does parameter 13). A major source of ambiguity in this approach is that the presence of the photosynthetic and photoprotective carotenoid pigments are also strongly absorbing energy in this spectral region, and can have large variations in their concentrations relative to Chl *a.* The equation for computing Parameter 14, chlor_MODIS is:

Log Total Chl *a* = $-1.594 (b9/b12))^3 + 1.122 (\log (b9/b12))^2 - 1.396 \log (b9/b12) - 0.0922$

The regression statistics for this analysis are: number of observations, n = 93 , coefficient of variance $r^2 = 0.915$, and the standard error of estimate Sy•x = 0.053, k = 1.

Product 15 - This total pigment product is based on the summation of the suite of phytoplankton pigment compounds measurable by HPLC. A list of compounds included (when present) in the totals is found in Table 1, along with their *in vitro* absorption peaks , spectral range and relative importance. The relative importance scale (which ranges from 1-7) is based on the frequency of occurrence and concentration within a pigment group. The top two groups absorb in a broad spectral range between 350-540 nm with their primary absorption peaks lying between 410-480 nm. It is for this reason that the initial MODIS total pigment algorithm utilized the ratio of the sum of all the nL_w(412, 442, & 487) bands (b8, b9, & b10) to the nL_w(547) band (b12) to cover as much of the absorption range as possible with MODIS. However, the MODIS band 8 has been temporarily removed from this ratio pending an improvement in the accuracy of the retrievals. The removal of b8 resulted in a slight reduction in r^2 from 0.946 to 0.934 and the standard error of estimate increased from 0.032 to 0.039. The present regression uses the ratio of the b9 and b10 sums to b12 and the total of the HPLC pigments in conjunction with the ATBD modifications discussed above.

The equation for computing Product 15, pigment_c1_total is:

Log Total Pigments = $-3.848 (\log(b9+b10)/b12))^3 + 6.106 (\log (b9+b10/b12))^2$
$- 4.250 \log (b9+b10-/b12) - 0.0922$

The regression statistics for this analysis are: number of observations, n = 93 , coefficient of variance $r^2 = 0.934$, and the standard error of estimate Sy•x = 0.0395, k = 1.

Results of a recent study pertaining to the global relationship between Chl *a* and accessory pigments can be found in Trees *et al*. (2000).

Table 1. HPLC Measured Pigments included in the Total Pigment Product.

Pigments	*Abs. Peak	*Abs. Peak	Range	** Importance
Chlorophylls				
Chlorophyll a	430	662	350-450	1
Divinyl Chlorophyll a	436	661	350-460	1
Chlorophyll b	457	645	410-480	3
Divinyl Chlorophyll b	460	644	405-490	3
Chlorophyll c1	446	628	400-470	2
Chlorophyll c2	450	581	410-475	2
Chlorophyll c3	452	586	410-485	2
Phaeopigments				
Pheophytin a	410	666	350-440	3
Pheophorbide a	410	666	350-440	2
Chlorophyllide a	431	664	390-450	1
Pheophytin b	434	653	400-460	5
Pheophorbide b	435	654	400-460	4
Chlorophyllide b	458	646	410-480	6
Photosynthetic Carotenoids				
19'-Butanoyloxyfucoxanthin	444	470	370-520	3
Fucoxanthin	446	468	340-540	1
19'-Hexanoyloxyfucoxanthin	444	470	360-520	2
Peridinin	458	474	360-550	4
Prasinoxanthin	451		360-540	5
Photoprotective Carotenoids				
Alloxanthin	454	484	360-520	3
Diadinoxanthin	448	478	360-500	1
Diatoxanthin	454	482	370-510	5
Dinoxanthin	442	471	350-500	6
ε,ε-carotene	440	470	350-500	3
ß,ß-carotene	454	480	360-510	3
Lutein	448	476	360-510	2
Neoxanthin	439	487	360-490	7
Violaxanthin	442	472	360-500	4
Zeaxanthin	454	481	370-510	2

*Absorbance maxima wavelength (nm) as measured in acetone, which results in a small shift to shorter wavelengths when compared to *in vivo* absorption.
** Importance - Frequency of occurrence and concentration within a group.

Data Accuracies

The uncertainty in these phytoplankton pigment determinations is the quadrature sum of the uncertainties in the nL_w ratios determined from MODIS radiances and in the regression relationship derived from in-water measurements. Several components of the uncertainty budget for satellite nL_w at a single wavelength, are associated with terms in the atmospheric correction. Many of these atmospheric terms will deviate from actual values in the same direction at all wavelengths. For example, a mismatch of aerosol optical thickness and its wavelength dependence will either increase or decrease the derived nL_w at all wavelengths. A ratio involving nL_w's at different wavelengths will then have less uncertainty from these types of uncertainty sources than do the individual nL_w's. The same will not be true for cases where one band may be biased to the negative and the other in a positive direction (i.e. large polarization uncertainties in the blue bands relative to a longer wavelength band (547 nm). Examples of these cases can be observed in Figure 3a and 3b in which the MODIS total band nL_w's as a function of the MODIS view angles are plotted for two of the data processing versions. This data set was produced for evaluating MODIS calibration for the Side B electronic configuration. The MODIS nL_w's were extracted for the MOBY site location off the coast of Lanai, Hawaii. Linear least squares regression results on the data sets demonstrated a large east to west bias in band 8 (412 nm), with the western nL_w's being too low. These slope bias trends decrease with increasing wavelengths in the blue, with the trends being reversed for the green-red bands. These biases resulted in pigment products being under-estimated on the eastern side and over-estimated on the western side of the swath. This effect produced systematic discontinuities between adjacent orbits. The magnitude of the bias was significantly reduced in processing version 3.2.1 after changing polarization models and recalibrating by Univ. of Miami personnel.

MOBY data is being utilized as a component of the vicarious calibration process required for ocean color satellite missions (Clark *et al*., 1997). MODIS overpass data over the MOBY site is available every 14 out of every 16 days at 14 different satellite zenith angles. For each day in which data are available, the exact daily GPS location for the MOBY buoy is matched with the nearest pixel on the HDF file. Data is extracted in a 3 km by 3 km grid around that nearest point, including geolocation, nL_w's (412 - 678 nm), data quality rating, mirror side, detector number, satellite and solar zenith and azimuth angles, atmospheric tau and epsilon, and aerosol model used.

This match up data set was also used to evaluate the prominent spectrally dependent east-west trends and accuracy in the nL_w 's retrievals. The percent differences between MOBY and MODIS total band radiances for bands 8, 9, 10, and 12 are presented in Figure 4a & b for the two processing versions. MODIS retrieval differences, when validated against MOBY and MOCE data illustrate

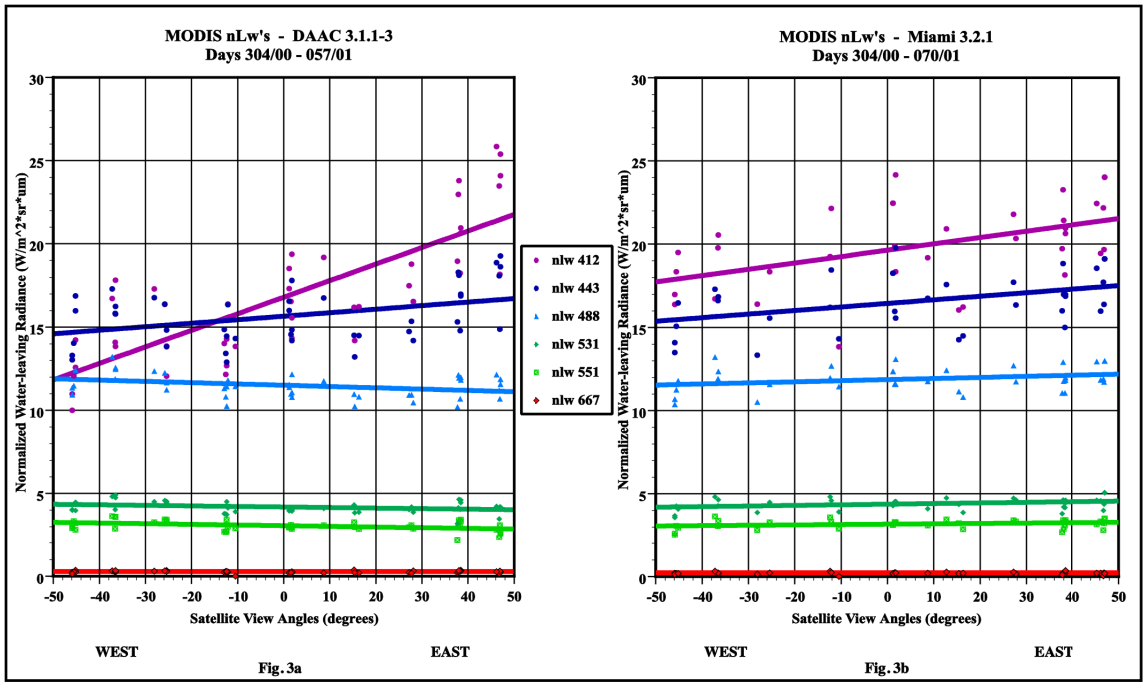

Figure 3. MODIS total band nL_W's for the view angle ranges between +- 50 degrees. Linear least- squares are included for each spectral band. Observations span the period between days 304, 2000 to 070, 2001. Fig. 3a and 3b are for the data processing versions 3.1.1 and 3.2.1.

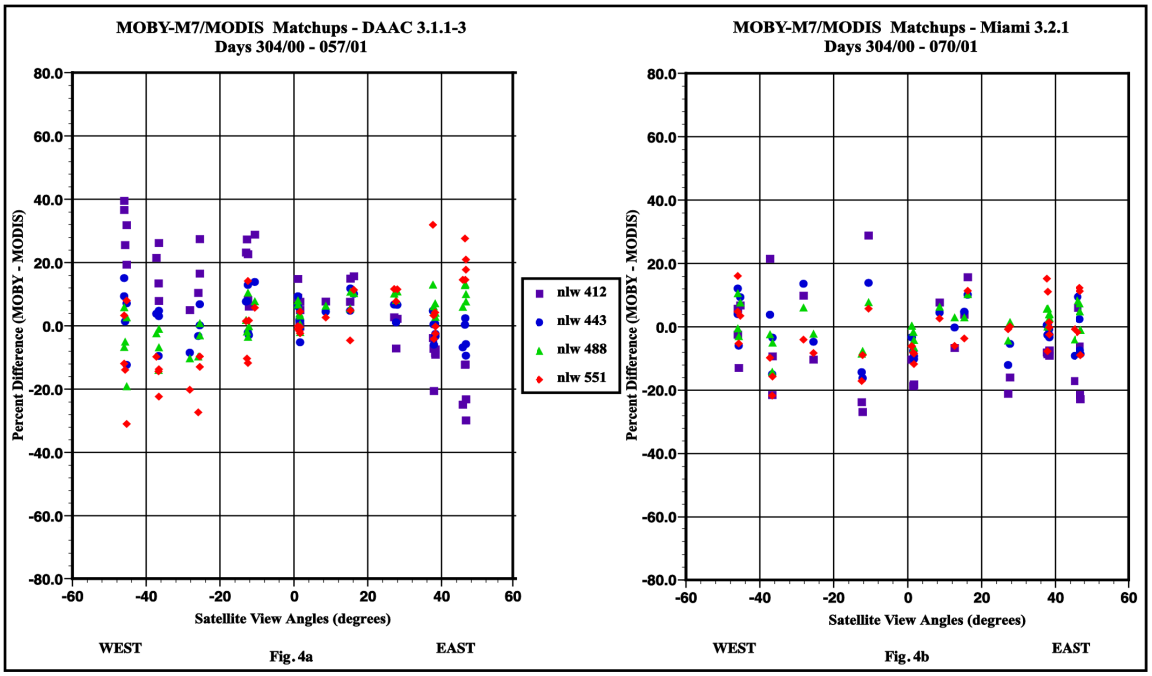

Figure 4. Percent differences between MOBY and MODIS nL_W match-up observations for spectral bands 8, 9, 10, and 12. Fig. 4a and 4b are for the data processing versions 3.1.1 and 3.2.1.

that the shorter wavelengths were too low west of nadir and too high east of nadir with less difference occurring east of nadir. Similar match-up data sets are being compiled for the other MODIS operating perturbations and configuration changes.

Validation - Initial Results

Since the launch of NASA's TERRA satellite, the Marine Optical Characterization Experiment (MOCE) Team has continued to acquire and provide at-sea observations for MODIS initialization, calibration, and product validation tasks. During this period, the team conducted eight field campaigns in Hawaii in conjunction with the maintenance of the MOBY systems. During four of these cruises, (MOCE-6, MOBY-L69, MOCE-7, and MOCE- 8) complete sets of the bio-optical, atmospheric, and physical oceanographic parameters were acquired. Data from the MOCE-7 cruise, conducted in December 2000, were used as an initialization data set for MODIS Side B electronics mode. Products for day 345 cruise were computed and the ship track from day 344 to 345 have been selected as an example for comparisons. This track and station 6 and 7 locations are shown below in Figure 5, superimposed on the CZCS_pigment concentration.

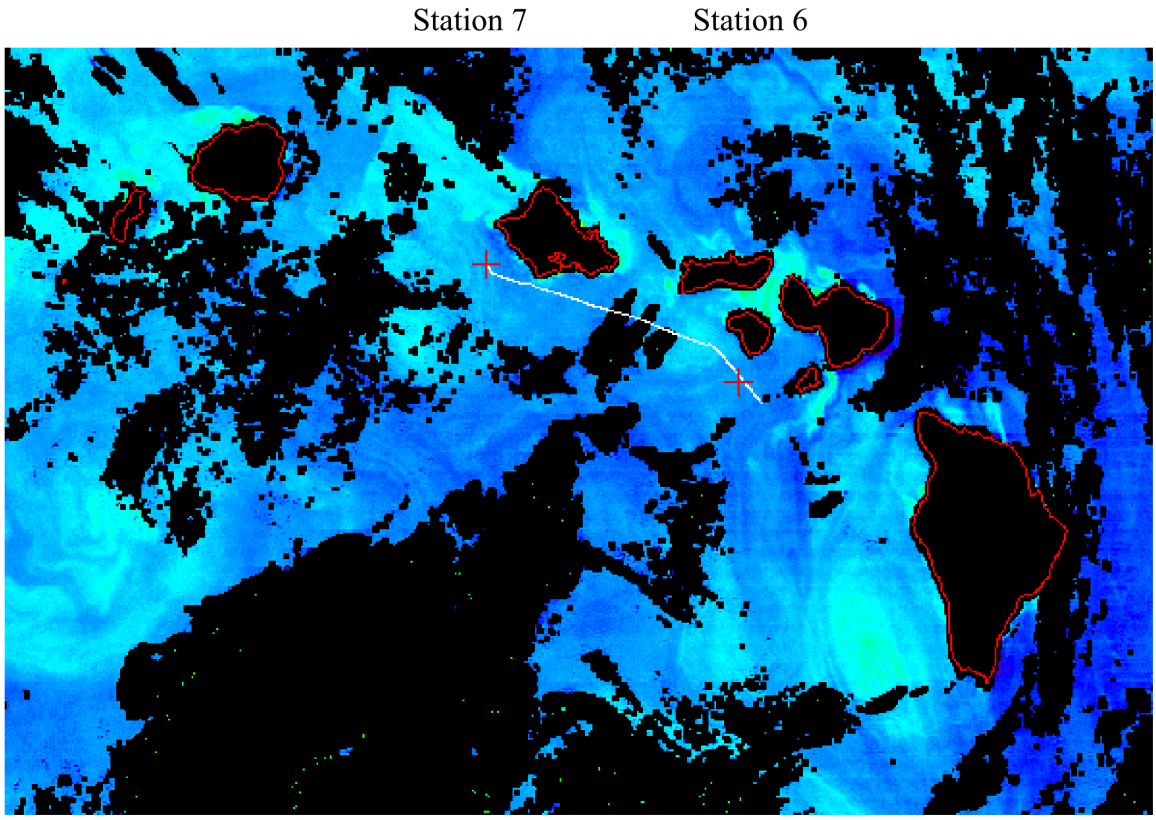

Figure 5. MOCE-7 station locations (+) and the R/V Ka'imikai-o-Kanaloa track (white) superimposed on the CZCS_pigment concentration (parameter 13) for yearday 345, 2000 (station 7).

The ship track started southeast of station six and terminated at station seven approximately 3 hours prior to the MODIS overpass. The CZCS_pigment and chlor_MODIS parameters are compared to the shipboard pigment concentrations in Figure 6. Shipboard flow-through fluorescence measurements were converted to pigment concentrations by a least-squares regression of laboratory-analyzed discrete samples to shipboard fluorescence.

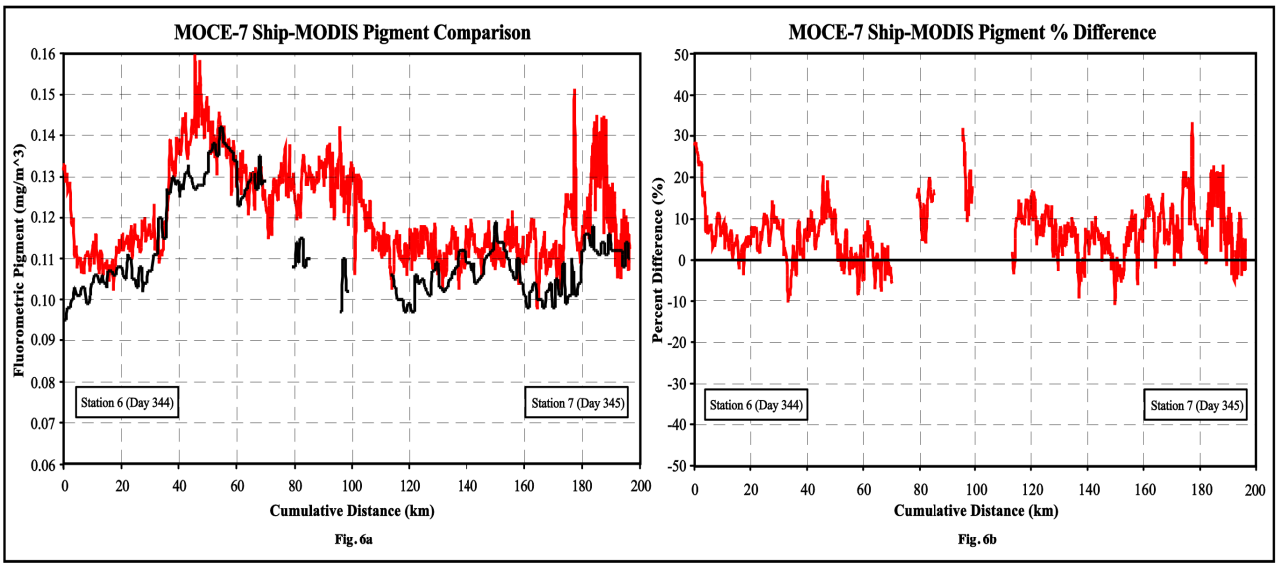

Figure 6. Comparison between the ship-measured pigments and the MODIS derived pigments and the along-track percent differences between ship and satellite (shown in Fig. 5). Figs. 6a and 6b are the comparisons for the CZCS_pigment and Figs. 6c and 6d are for the chlor_MODIS parameters.

The comparison plots for the CZCS_pigment and chlor_MODIS parameters are depicted in Figs. 6a & 6c with their respective percent differences (ship-MODIS) plotted in Figs. 6b & 6d. The pigments retrieved for the fluorometrically determined CZCS_pigment shows on the average an 8% underestimate between the ship and MODIS values. An offset is present in the HPLC derived chlor_MODIS as well, where the total Chl *a* is underestimated by approximately 10 to 15% over the track. Part of the offsets in these comparisons can be accounted for by some small errors known to be present in the pigment databases used to formulate the regression results. However, these initial validation results are very encouraging and demonstrate a vast improvement over the retrievals before the vicarious calibration corrections were applied.

Thresholds and Product Quality Level Flags

Product quality flags range from 0-3. Flags are assigned only when the nL_w 's are computed and the quality level indicates no know problems (flag = 0). The product thresholds, ranges and associated uncertainties for the quality level flags for these products are:

1. **If** nL_w's (b9, b10, b11, & b12) = -1 **or** the nL_w quality flag is not zero: **then** all products = -1; and QC flag = 3.

2. **If** product (13, 14, & 15) values are < 0.01 mg/m^3 (ug/l) or > 100 mg/m^3 (ug/l): **then** Product = -1: and QC flag = 3.

3. **If** product (13, 14, & 15) = 0.01 and is < 0.05 mg/m^3 (ug/l): **then** QC flag = 2. [High probability of Case 1 waters, higher uncertainty in the nL_w retrieval accuracy].

4. **If** product (13, 14, & 15) = 0.05 and is < 2.5 mg/m^3 (ug/l): **then** QC flag = 0. [High probability of Case 1 waters, lowest uncertainty in the nL_w retrieval accuracy].

5. **If** product (13, 14, & 15) = 2.5 and is < 25 mg/m^3 (ug/l): **then** QC flag = 1. [High probability of a mix of Case 1 and Case 2 waters, higher uncertainty in the nL_w retrieval accuracy].

6. **If** product (13, 14, & 15) = 25 and ≤ 100 mg/m^3 (ug/l): **then** QC flag = 2. [Highest probability of Case 2 waters, highest uncertainty in the nL_w retrieval accuracy].

Status and Planned Improvements

The vicarious calibration of MODIS is a challenging process that has been and will continue in the near future to be a series of iterations. The user is advised to be cognizant of these changes by checking the MODIS home page for known problems and revisions. The most recent processing for the MODIS Side B electronics, version 3.2.1, is producing the highest quality products to date and it

is recommended to use version 3.2.1 or higher. It is advisable, if using earlier products, to restrict use to viewing angles of ± 25 degrees. Currently it is believed that version 3.2.1 is underestimating the CZCS_pigment concentrations in the southern hemisphere (retrievals in the 0.01- 0.02 mg/m^3 range) as a result of selecting the appropriate approximation of zero (in log space), for the HRG pure water nL_w ratio. This problem has been solved and will be corrected in the next processing version.

Version 3.2.1 may have a residual east west bias for bands 8 & 9 which appears to be more prevalent in the southern hemisphere. Additional match up data are being acquired for analysis before further modifications are recommended.

Since MODIS is now operating on Side A electronics a re-initialization process will be required. A MOCE cruise is now planned for December 2001 to provide a data set for Side A initialization. A MOBY match-up data base will be produced as Side A data becomes available.

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